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Graphene oxide/N-methyl-2-pyrrolidone charge-transfer complexes for molecular detection

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ABSTRACT

Charge transfer complex (CTC) has been formed between photoluminescent graphene oxide (GO) as electron acceptor and N-methylpyrrolidone (NMP) as electron donor. Studies of UV absorption and photoluminescence (PL) suggest that the formation of CTC results in a red-shift of absorption and a new PL emission. Decay dynamics was described by time-resolved PL spectra and a clear ultrafast charge-transfer process was observed from the PL rise times. The PL of the CTC was sensitive to external components, allowing molecular detection of 7,7,8,8-tetracyanoquinodimethane and 1,3,5-trinitrobenzene up to hundred nanomolar concentration levels through the photoluminescence signals.

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1. Introduction

Graphene oxide (GO) is an atomic two-dimensional network consisting of sp^2 and sp^3 carbon bonds that is partially modified with covalent oxygen functional groups on the basal plane or at the edges [1–3]. Its unique molecular structure has interesting optical and chemical properties that give it applicability in various fields such as optics [4–7], drug delivery [8,9] and biosensors [10,11]. Unlike graphene, with its ideal sp^2-bonded lattice structure that lacks an energy gap [12], GO possesses a finite electronic band gap originating from the disruption of the π networks [4–7]. It therefore exhibits photoluminescence in the near-infrared (NIR), visible, and near ultraviolet regions [4–8]. Optoelectronic properties are generally determined by the π states of sp^2 sites in carbon materials with mixed sp^2 and sp^3 bonding [13,14]. Localized finite-sized sp^2 clusters within a sp^3 matrix can confine π-electrons in GO [4–7]. Photoluminescence is attributed to the recombination of electron–hole pairs in localized electronic states in nanoscale GO of various sizes and shapes [4–7].

Carbon nanotubes (CNTs), fullerene (C60), and graphene are good electron acceptors due to their sp^2-hybridized carbon bonds and charge-transfer can occur easily between organic molecules and these carbon materials [15–26]. The formation of charge-transfer complexes (CTCs) between CNTs and aniline has been reported to enhance the quantum yield and the solubility of CNTs [15]. Charge-transfer between fullerene derivatives and organic molecules has also been widely studied [16,19], especially in organic solar cell systems [18,19]. Chemical-modified graphene from GO was applied to organic solar cells as a novel electron acceptor [20,21]. Graphene sheets can be doped with electrons through charge-transfer with organic molecules, resulting in modified electron and hole concentrations and modified electronic properties [22–26]. Recently, photophysical properties of CTCs between various electron-donating molecules and photoluminescent GO have also been reported by our group [27].

Encouraged by the previous results, we have reported the charge-transfer interaction between GO and electron-donating N-methylpyrrolidone (NMP) investigated through the analysis of UV absorption and PL in this work. Furthermore, it is found that the PL emission from the GO-NMP CTCs was sensitive to the concentration of external organic molecules, allowing molecular detection of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 1,3,5-trinitrobenzene (TNB) at extremely low concentrations through the CTCs' photoluminescence signals. To the best of our knowledge, this is the first time to report the effect of interaction of electron-donating molecules on the photophyslcal properties of GO and the CTC formation based on GO.

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2. Experimental

2.1. GO synthesis and quantitative molecular analysis

GO sheets were prepared efficiently by microwave-irradiated expansion of graphite oxide followed by solution exfoliation, as described elsewhere [28]. Pristine natural graphite flakes (10 mesh, 99.9%, Alfa) were mixed with concentrated sulfuric acid (98 wt.%) and hydrogen peroxide (30 wt.%). After wash with deionized (DI) water to pH neutral, the graphite oxide was expanded in a microwave oven at 750 W for 10 s. Five milligram expanded graphite oxide was dispersed in 50 ml DI water and sonicated by a tip sonication instrument at 500 W for 10 h. A well-dispersed GO solution was obtained after centrifugation at 13,000 rpm. To obtain luminescent GO, the centrifuged supernatant was filtered through a 0.2-μm microporous membrane. After a lyophilization for 2 days, GO powder was obtained. The solid GO was dispersed in water and NMP with concentration of 0.01 mg/ml and characterized by UV–vis and PL spectra. 7,7,8,8-tetracyanoquinodimethane (98%, Aldrich) and 1,3,5-trinitrobenzene (analytical standard, Aldrich) were added to the GO-NMP solution with different concentrations; after that, PL spectra of the GO-NMP solution were measured to test the molecular sensing capability of GO-NMP CTC.

2.2. Materials characterizations

Elemental analysis for GO was done by X-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech, England) with twin anodes, Al $K\alpha$ (1486.6 eV) and Mg $K\alpha$ (1256.6 eV). Sample was prepared by spin coating a uniform GO film from water on a silver pre-coated Si substrate. Wide scan spectra were recorded at 50 eV pass energy while the narrow scan spectra were recorded at 20 eV pass energy. These give the analyzer energy resolutions as ±1 and 0.4 eV, respectively. Assuming a Gaussian line shape, the XPS peaks were resolved into individual components after proper subtraction of baseline by using Shirley background subtraction method with the help of software supplied by V.G. Microtech.

PL and UV absorption analyses were carried out with a FP-6200 Spectrofluorometer and a V-630 Bio UV–vis Spectrophotometer. Spectra were measured at room temperature in quartz cells (1 cm path length). All of the spectra were reproduced. Data analysis was performed by using spectra manager provided by JASCO. Time-resolved PL measurement was carried out using a frequency-doubled, femtosecond pulsed Ti:sapphire laser at an excitation wavelength of 350 nm and a time-correlated single photon counting detection system.

3. Results and discussion

The atomic composition of GO obtained from X-ray photoelectron spectrum (Fig. 1) shows a C:O ratio of 2.6:1, which is slightly higher than that of GO obtained from conventional methods [29]. The UV–vis absorption of the GO in water and NMP is shown in Fig. 2(a). The comparison showed that the absorption curve was red shifted to longer wavelengths when solid GO was dispersed in NMP. At the same time, two solutions with the same concentration showed different colors: the aqueous GO dispersion was colorless and transparent; however, the GO-NMP solution with the same concentration was bright brown (Fig. S1 in supplementary material). The unpaired electrons of the amidic nitrogen atom make NMP a good electron donor; it has been reported to generate CTC with fullerene (C_{60}) [30–32]. Meanwhile, Fullerene and CNTs have also shown ground state interactions with various aromatic amines that are attributable to electron transfer from the amines to the fullerenes or CNTs [15–17]. Chemically modified graphene (from GO) has been used in organic solar cells as an electron acceptor [20,21]. The sp^2 domains/clusters dispersed in GO sheets are structurally similar to fullerenes and CNTs, making GO a good electron acceptor. The red-shift of UV absorption and the bright brown color of the solution suggest the formation of the GO-NMP CTC, which formed through the charge-transfer [15,16,27,33]: GO accepted electrons donated by NMP.

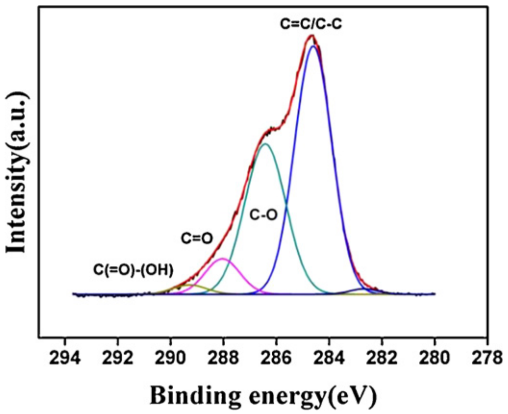

Fig. 1. XPS C 1s spectra of GO.

In Fig. 2(b), two PL emission peaks show on the PL spectra from the GO-NMP solution. The maximum peak emission is at 409 nm, with a shoulder peak at 475 nm. This is in contrast to the single PL peak observed from aqueous dispersed GO (Fig. 2(b)), which is attributable to the recombination of electron-hole pairs in localized electronic states in the GO sheets [4,5]. Similar dual PL behavior has also been observed in CNT-aromatic amine [15] and C_{70}-N, N-diethylanilne CTC [16]. The formation of CTC caused a second PL emission located at longer wavelength [15,16]. Accordingly, the luminescence band at 475 nm is attributed to the excited state of the GO-NMP CTC. The intensity of this emission was relatively high, with respect to the 409 nm band, indicating the CTC's considerable PL quantum yield. Interestingly, the PL emissions vary with different solvents. Fig. 2(b) shows the emission spectra of the solid GO dispersed in various solvents with different polarities, including water, NMP, mixtures of NMP with toluene, acetone, and methanol at a volume radio of 3:1. Increasing solvent polarity decreases the 475 nm quantum yield relative to the 409 nm emission. The GO-NMP CTC can easily be disassembled in highly polar environments; the complexes' instability in highly polar solvents accounts for the decrease in the longer wavelength emission.

Time-resolved PL measurements were carried out to figure out the decay mechanism of PL emissions. Fig. 3(a) shows the room temperature PL decay times of the 409 nm and 475 nm emissions from the GO-NMP solution. The two emissions showed different decay dynamics, reflecting different excited states [34]. Decay dynamics was modeled as the summation of two exponential functions, as is to be expected with two excited species (see details in Supplementary material). The major component associated with 409 nm emission has a decay time of 0.99 ns with 97%. However, the 475 nm emission exhibited much longer decay times: 2.36 ns with 88% and 9.86 ns with 12%. The longer decay time for the 475 nm emission accorded with the CTC formation in this solution [34,35]. Fig. 3(b) shows the PL rise times detected at the two emission wavelengths. The 475 nm emission took 40 ps longer to reach peak intensity than the 409 nm emission. The delayed rise time of the 475 nm emission indicates the ultrafast charge-transfer between excited NMP and GO within 40 ps.

Due to a high surface area to volume ratio and unique properties of graphene and GO, they have been broadly studied and applied to the detection of chemical and biological molecules and pH

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